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Variations in lattice parameters with annealing temperature for L-Pd_5Ce

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Abstract

The lattice parameters of L-Pd_5Ce have been determined as a function of annealing temperature. L-Pd_5Ce has a one-dimensional long-period superstructure derived from $L1_2$, and the long periodic direction is along [110] of the $L1_2$ lattice. At 873 K, the distance between adjacent anti-phase boundaries, or the domain size, is almost exactly $M=3$ in units of the lattice spacing of (110) planes of $L1_2$ $(=c_0)$, and the crystal structure is *Pmma* with the lattice parameters $a=0.5700$ nm, $b=0.4062$ nm and $c=3c_0=0.8462$ nm. The axes correspond to $[\bar{1}10]$, [001] and [110] respectively of $L1_2$. When M is even, the space group of the structure is regarded as *Bmmm* for the above setting of the axes. As the annealing temperature is elevated to 973 K, the quantities $a/2^{1/2}$, b and $2^{1/2}c_0$, which correspond to the lattice dimensions of the pseudocubic lattice of $L1_2$, then have an identical value to one another. The variation in lattice parameters is explained in terms of a rapid increase in M associated with atomic disordering. The observed lattice parameters indicate that the averaged atomic volume varies less than 0.2%. The small variation cannot be a cause of the distinct dependence of electrical resistivity upon the annealing temperature.

1. Introduction

It is well known that alloys and compounds of cerium exhibit distinct anomalies in physical properties such as electrical resistivity. The anomalies are attributed to the mixed valence of cerium. The present authors [1] found that the magnitude of the anomalies shows a strong dependence on annealing temperature for Pd_7Ce, L-Pd_5Ce and Pd_3Ce. Since these phases are of ordered structures [2–5], the annealing temperature dependence is thought to be due to changes in the degree of order. Actually, the degree of order in Pd_7Ce and L-Pd_5Ce was confirmed to vary with annealing temperature [6, 7]. The change in degree of order can affect the atomic distances, the atomic volume and so on, which are possible causes of the annealing temperature dependence. In the case of L-Pd_5Ce, the temperature coefficient of electrical resistivity

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below room temperature and the value of the resistivity at room temperature show distinct changes with annealing temperature between 873 and 973 K [1]. Since the physical properties of cerium alloys are well described as a function of Ce–Ce distance and/or lattice parameters [8, 9], crystallographic data are required to discuss the effects of 4f electrons on the annealing temperature dependence. However, there has been no intensive work on the lattice parameters of L-Pd_5Ce. In this study, the lattice parameters of L-Pd_5Ce have been determined as a function of annealing temperature in order to supply the crystallographic data.

2. Experimental procedure

An ingot of Pd–16.7at.%Ce was made by melting elements of palladium and cerium in an arc furnace under an atmosphere of extra-pure argon. The weight loss after melting was negligibly small so that the deviation in composition from the stoichiometry was believed to be less than ± 0.2 at% Ce. The alloy ingot was filed to powder under an atmosphere of argon, and annealed in vacuum at various temperatures between 873 and 973 K for 172.8 ks (873–913 K) or 86.4 ks (933–973 K), followed by quenching into iced brine. X-ray diffraction patterns for the powder specimens were recorded with a conventional diffractometer with nickel-filtered Cu Kα radiation. Annealed powder of palladium (the lattice parameter $a = 0.38906$ nm) was used to calibrate the diffraction angles. The conditions for measurement were as follows; the scanning speed was 1.45444×10^{-4} rad s^{-1} (0.5° min^{-1}) in 2θ and the time constant was 2 s for the specimen annealed at 873 K, and 1° min^{-1} and 1 s for the other specimens. The powder pattern was calculated for L-Pd_5Ce using the atomic scattering factors of palladium and cerium given by Smith and Burge [10]. The temperature factor was not taken into account, for no reliable data for it were available.

A disc specimen 3 mm in diameter was prepared and heat treated in the same way as for the powder specimens. The disc specimen was electrothinned to electron transparency in a solution of LiCl, $Mg(ClO_4)_2$ and CH_3OH. Electron microscope observation was made with a JEM-2000FX microscope.

3. Results and discussion

3.1. *Crystal structure of L-Pd_5Ce*

Figure 1(a) illustrates the crystal structure of L-Pd_5Ce type [4] which is a one-dimensional long-period superstructure derived from $L1_2$ by inserting periodic anti-phase boundaries (APBs) with a shift vector of $\frac{1}{2}[110]_{L1_2}$, where the subscript $L1_2$ means that the indices are referred to $L1_2$. The structure is regarded as orthorhombic with the axes $a \| [\bar{1}10]_{L1_2}$, $b \| [001]_{L1_2}$ and $c \| [110]_{L1_2}$. As the length of the c axis in the present structure

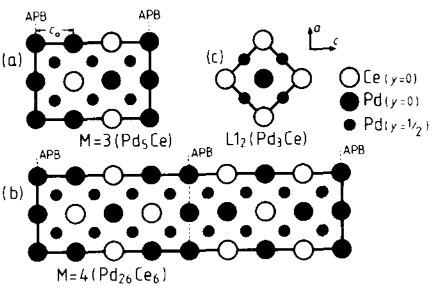

Fig. 1. Crystal structures of L-Pd_5Ce type (○, Ce ($y=0$); ●, Pd ($y=0$); •, Pd ($y=\frac{1}{2}$)): (a) $M=3$ (Pd_5Ce); (b) $M=4$ ($Pd_{26}Ce_6$); (c) $M=\infty$ or $L1_2$ structure (Pd_3Ce). The compositions in parentheses represent the ideal ones of the structures. Deviations from Pd_5Ce can be compensated by atomic disordering.

TABLE 1

Coordinates of the sites in the L-Pd_5Ce structure

Site	Coordinates
Ce	$(\frac{1}{2}, 0, \frac{1}{3}+z_c)$
	$(0, 0, \frac{2}{3}-z_c)$
Pd	$(0, 0, z_1)$
	$(\frac{1}{2}, 0, -z_1)$
	$(\frac{1}{4}+x_2, \frac{1}{2}, \frac{1}{6}+z_2)$
	$(\frac{3}{4}-x_2, \frac{1}{2}, \frac{1}{6}+z_2)$
	$(\frac{1}{4}-x_2, \frac{1}{2}, \frac{5}{6}-z_2)$
	$(\frac{3}{4}+x_2, \frac{1}{2}, \frac{5}{6}-z_2)$
	$(0, 0, \frac{1}{3}+z_3)$
	$(\frac{1}{2}, 0, \frac{2}{3}-z_3)$
	$(\frac{1}{4}, \frac{1}{2}, \frac{1}{2})$
	$(\frac{3}{4}, \frac{1}{2}, \frac{1}{2})$

is the distance between adjacent anti-phase boundaries, it is conventionally represented in units of the spacing of the basic order lattice planes, $c=Mc_0$, where c_0 is the lattice spacing of $(110)_{L1_2}$ planes. The structure of L-Pd_5Ce annealed below 873 K has an M value of 3 (Fig. 1(a)). The numbers of cerium and palladium sites in the unit cell are two and ten respectively, and their coordinates are given in Table 1, where x_i and z_i are small deviations from their rational positions. Shifting the origin of the coordinates by ($\frac{1}{4}$, 0, $\frac{1}{2}$), one can easily see that the structure has an inversion centre and the space group *Pmma*. The value of M can increase with increasing cerium content and temperature [7]. For M even, the axis c should be $2Mc_0$, as shown in Fig. 1(b), in order to maintain the orthorhombic symmetry, and then the space group is *Bmmm* for the above setting of axes. Alternatively, if one wants to set common axes which present the long period by $2M$ in a conventional way for both M odd and M even, the lattice should be regarded as monoclinic [4].

Figure 2 shows an electron diffraction pattern for L-Pd$_5$Ce with $M \approx 3$. Diffraction spots indexed as $hk0_{L1_2}$ with $h+k$ odd should vanish owing to the anti-phase structure. However, spots sometimes appear at such positions as indicated by arrows in Fig. 2. It is noted that the position of the spot deviates from the symmetrical point. The spots are assigned as $hkl = 00l$ with $l =$ odd, or its equivalent, of another orientation variant with $c \parallel [101]_{L1_2}$ or $c \parallel [10\bar{1}]_{L1_2}$, and the deviation in position is due to the distortion of the basic L1$_2$ lattice. From close examination of the deviation of the diffraction spots, the L1$_2$ lattice is found to be contracted by about 1% along $[\bar{1}10]_{L1_2}$ (a axis of the orthorhombic lattice) and 2% along $[110]_{L1_2}$ (c axis), relative to $[001]_{L1_2}$ (b axis).

Table 2 shows the results for the X-ray diffraction pattern of L-Pd$_5$Ce. Since the annealing temperature is 873 K, the value for M is thought to be 3. In a knowledge of the relative contraction of the L1$_2$ lattice along $[\bar{1}10]_{L1_2}$ and $[110]_{L1_2}$, or the a and c axes of the orthorhombic lattice, the values for the lattice parameters were determined by the least-squares method to be $a = 0.5700_4 \pm 0.0000_5$ nm, $b = 0.4062_2 \pm 0.0000_4$ nm and $c = 3c_0 = 0.8461_7 \pm 0.0000_7$ nm, yielding $a/2^{1/2}b = 0.992_2$ and $2^{1/2}c_0/b = 0.981_9$. Since the L-Pd$_5$Ce phase has a narrow concentration range for solid solution [7, 11], the above values for lattice parameters can vary with the alloy composition. The observed powder data are found to be in good agreement with the calculated data where x_i and z_i are assumed to be zero. One can see that the indices of the observed diffraction lines have an even value for h and a multiple of 3 for l. A set of the reduced indices $h/2$ k $l/3$ naturally satisfy an extinction rule for a body-centred lattice, indicating that they are

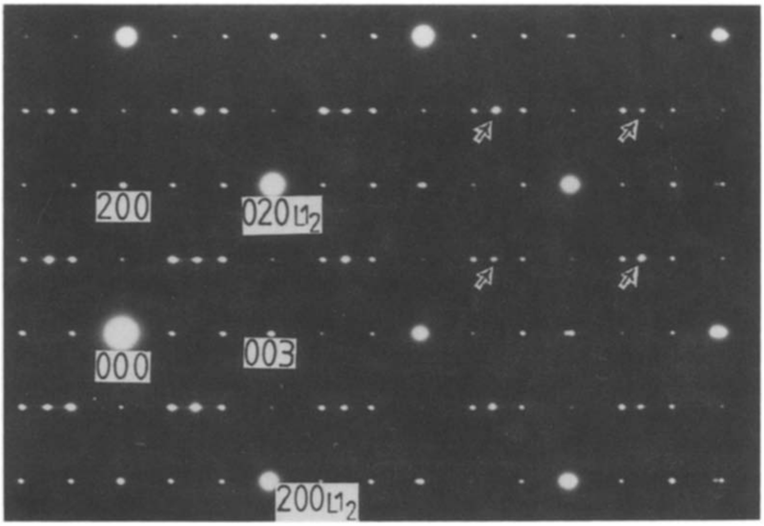

Fig. 2. Electron diffraction pattern for L-Pd$_5$Ce with $M \approx 3$. The indices with the subscript are referred to L1$_2$ and those without it to the orthorhombic lattice. It is noted that the diffraction spots at hkl_{L1_2} with $h+k$ odd, as indicated by the arrows, deviate from the symmetric positions.

TABLE 2

X-ray powder data for L-Pd_5Ce

Observed[a]		Calculated[b]			
d (nm)	I/I_0	*d* (nm)	I/I_0	*hkl*	hkl_{L1_2}[c]
		0.846_2	<1	001	
		0.4728	<1	101	
		0.3081	<1	111	
0.2332	100	0.2333	100	210	$1\bar{1}1$
0.2318	95	0.2317	98	013	111
0.2030	30	0.2031	33	020	002
0.2006	60	0.2005	63	203	200, 020
0.1426[d]	50	0.1427	41	223	022, 202
		0.1425	10	400	$\bar{2}20$
0.1410	10	0.1410	10	006	220
0.1223_2	12	0.1223_0	12	230	$1\bar{1}3$
0.1220_6	15	0.1220_7	12	033	113
0.1214_0	20	0.1213_9	24	413	$3\bar{1}1$, $1\bar{3}1$
0.1206_9	18	0.1207_0	24	216	131, 311
0.1166_4	12	0.1166_6	11	420	$\bar{2}22$
0.1158_3	10	0.1158_5	10	026	222
0.1015_5	5	0.1015_6	4	040	004
0.1002_5	8	0.1002_4	8	406	400, 040
0.09270_3	12	0.09271_1	15	433	$\bar{1}33$, $3\bar{1}3$
0.09245[d]	20	0.09251_4	8	610	$3\bar{3}1$
		0.09240_3	15	236	133, 313
0.09158_2	5	0.09160_6	8	019	331
0.09060_1	15	0.09059_7	16	243	024, 204
0.09002_9	10	0.09004_1	8	603	$\bar{2}40$, $4\bar{2}0$
0.08990_6	12	0.08989_6	16	426	042, 402
0.08929_0	5	0.08929_5	8	209	240, 420

[a] Pd–16.7at.%Ce annealed at 873 K.

[b] L-Pd_5Ce with $M=3$, $a=0.5700_4$ nm, $b=0.4062_2$ nm, $c=0.8461_7$ nm, $x_i=z_i=0$ and $M=3$. Weak lines with $I/I_0<0.5$ are omitted.

[c] Corresponding indices referred to $L1_2$.

[d] Broad line.

fundamental lattice reflections of the orthorhombic lattice indicated in Fig. 1. These indices correspond to those referred to $L1_2$ listed in the right-hand column of Table 2. The order lattice reflections are expected to have quite small relative intensities I/I_0 less than 1%, so that they are hardly detectable with a conventional diffractometer.

In order to obtain the exact atomic distances in Ce–Pd and Ce–Ce pairs in L-Pd_5Ce, the deviations z_c, z_2, x_2 and z_3 in the coordinates of the atom sites from their ideal positions should be determined. However, as only the fundamental lattice reflections can be detected, the number of the observable reflections is very small. The observed reflections overlap each other so that it is quite difficult to determine a reliable intensity of the reflections. Our preliminary calculation, however, predicted that a value greater than 0.01 for z_i intensifies some reflections such as $hkl = 102$ and 113 up to $I/I_0 > 1\%$. Since no such reflections were actually detected by a careful examination, z_i and x_2 are thought to be almost zero or to have quite small values.

3.2. *Temperature dependence of lattice parameters*

Some of the present authors [7] reported that the value of M increases towards infinity with increasing temperature. The variation in M is explained in terms of atomic disordering. The crystal structure of L-Pd_5Ce with $M = \infty$ is regarded as $L1_2$ with a low degree of order, and is then expected to be cubic. Figure 3 shows the X-ray powder patterns for L-Pd_5Ce annealed at various temperatures between 873 and 973 K. It is seen that, as the annealing temperature is increased, a group of split diffraction lines are merged into a single line. The sharp profile of the diffraction lines from the specimen annealed at 973 K indicates that the structure is almost cubic, implying that M adopts a large value. The present result of the X-ray experiment is consistent with an electron microscope observation [7] that the value of M, which is 3 around 873 K, increases rapidly to about 8 at 973 K.

It is obvious that the basic $L1_2$ lattice of L-Pd_5Ce is distorted from a cubic system. However, if the specimen is not annealed well enough to reach its equilibrium state, there can exist certain fluctuations in M and/or the degree of order. Such fluctuations obscure the splitting of the X-ray diffraction lines, and then the powder pattern starts to resemble that of an f.c.c. lattice. Insufficient annealing can give rise to the misleading result that the structure of Pd_5Ce is essentially of a cubic system.

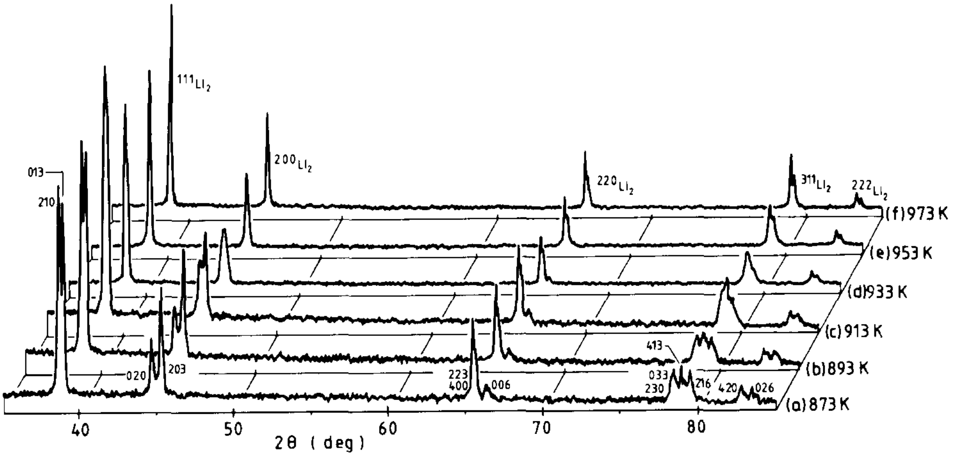

Fig. 3. Variation in X-ray powder pattern for L-Pd_5Ce with annealing temperature between 873 and 973 K. The indices with the subscript $L1_2$ are referred to the $L1_2$ lattice. Patterns (d)–(f) were reduced to one-half in the ordinate, relative to patterns (a)–(c).

Figure 4 shows the variations in the lattice parameters with annealing temperature. In order to indicate the change in dimension of the pseudolattice of $L1_2$, the values of $a/2^{1/2}$, b and $2^{1/2}c_0$ are plotted against the annealing temperature. The larger magnitudes of error of the data for 893–973 K, compared with those for 873 K, are caused by the fact that the positions of some overlapping diffraction lines could not be determined accurately. One can see in Fig. 4 that b decreases and $2^{1/2}c_0$ increases with annealing temperature, while $a/2^{1/2}$ decreases slightly. At 973 K, these parameters are almost identical to one another, indicating that the structure becomes close to being cubic. The value for b ($a/2^{1/2}$, $2^{1/2}c_0$) after annealing at 973 K gives the lattice parameter of the cubic lattice with no distortion as $a_{L1_2}=0.4026$ nm, in agreement with $a=0.4038$ nm [11], 0.4024 nm [12] and 0.403 nm [13] in the literature.

As above mentioned, the physical properties of L-Pd_5Ce exhibit a distinct dependence on annealing temperature [1] which is ascribed to the change in degree of order. The change in degree of order can alter the circumstances of cerium: the volume of cerium and the number of Ce–Ce nearest-neighbour pairs. These are possible causes for the annealing temperature dependence of the physical properties, and then it is important to clarify which component has a significant effect on it. Figure 4 also shows the variation in the averaged atom volume $\langle v \rangle$. It is seen that the magnitude of variation $|\Delta\langle v \rangle/\langle v \rangle|$ is less than 0.2%. As the magnitude is comparable with the accuracy of the data for 893–953 K, it is yet uncertain whether the observed variation is significant. According to a high pressure experiment [14], application of a pressure of 77 kbar increases the electrical resistivity of L-Pd_5Ce at room temperature by less than 10%, while the averaged atom volume decreases

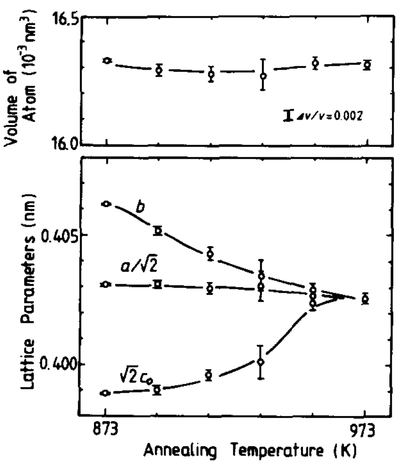

Fig. 4. Variation in the lattice parameters (top curve, b; middle curve, $a/2^{1/2}$; bottom curve, $2^{1/2}c_0$) and the averaged atomic volume with annealing temperature for L-Pd_5Ce. The scaling bar indicates $\Delta v/v=0.002$.

by 5%. Then the volume change of 0.2% is thought to induce the change of less than 0.4% in resistivity. This suggests that the change in lattice parameters of L-Pd_5Ce associated with annealing temperature gives little contribution directly to the large annealing temperature dependence of the electrical resistivity.

4. Conclusions

The lattice parameters of L-Pd_5Ce were determined as a function of annealing temperature in the range 873–973 K. The following conclusions can be drawn.

(1) L-Pd_5Ce with $M=3$ has an orthorhombic lattice with $a=0.5700$ nm, $b=0.4062$ nm and $c=3c_0=0.8462$ nm, yielding $a/2^{1/2}b=0.993$ and $2^{1/2}c_0/b=0.982$.

(2) As the annealing temperature is elevated, the lattice parameters vary in such a way that the fundamental $L1_2$ lattice becomes close to being cubic. The lattice dimension of the $L1_2$ is 0.4026 nm.

(3) The averaged volume per atom $\langle v \rangle$ in L-Pd_5Ce is almost constant, irrespective of annealing temperature.

Acknowledgments

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